ESRF	**Experiment title:** Sub-micronic in-depth microstructural evolution within functional piezoelectric (PbZrTiO3) MEMS: In-operando nanopencil beam diffraction approach	**Experiment number**: Ma2278
Beamline:	**Date of experiment**: from: 4/02/2014 to: 6/02/2014	**Date of report**: 10/09/2015
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Report

The aim of the experiment was to probe in-depth structural and micro-structural heterogeneities within the piezoelectric morphotropic Pb(Zr0.52Ti0.48)O3 (PZT) thin films during electric excitation. We used in-situ nano- pencil beam X-ray diffraction. This approach has indeed proved its efficiency to study in-depth microstructural gradient [1]. This first in-situ implementation has provided unique information within state of art functional polycrystalline PZT film elaborated in CEA-Leti.

Summary

The beamtime was very successful (only 9 shifs):

1. We succeed in fine structural depth profiling of the 1µm thick PZT layer [resolution 100nm].
2. We succeed to measure Z-scan during in-situ electric loadings for 3 differents samples (3 different elaboration process)
3. Bonus : we observed ''in-live'' dielectric breakdown and observed two damage modes. These unexpected results are very promising in endurance testing of our device.

The first point is under reviewing in *Appl. Phys. Lett.* Analysis and manuscrit preparation about point 2 are in good progress. Analysis of point 3 is beginning.

Sample preparation and Instrumentation achievements

We have developed a simple but efficient electric setup to perform in Operando experiment. Our Keighley voltage source is piloted directly from ESRF spec control software using the source GPIB output.

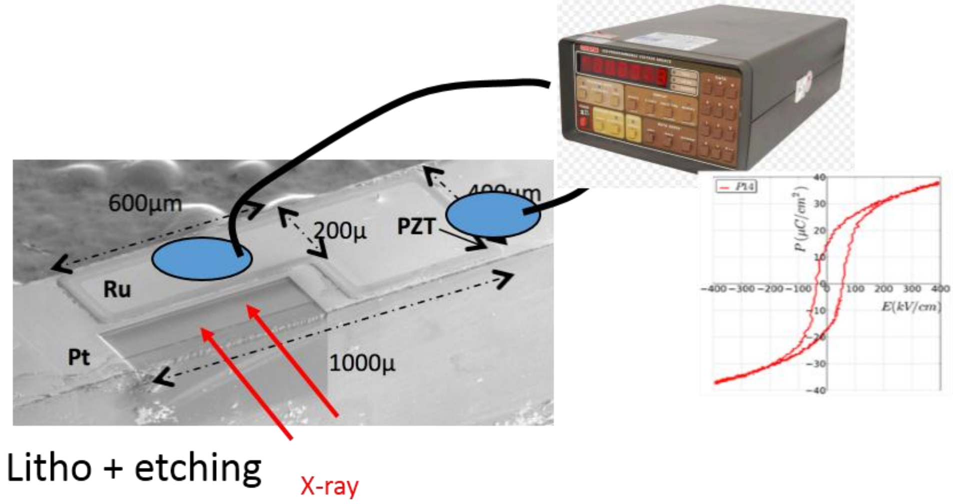

Fig 1 : MEB image of our PZT capacitor for In Operando experiments, elaborated in our clean-room platform. The voltage source is piloted into spec beamline control system.

1. In-depth Structurale Profilometry

Direct quantification of structural in-depth composition in lead zirconate titanate thin films (PZT) has been conducted using newly available X-ray nano-pencil beam (i.e. beam size of 100 nm x 50 µm) diffraction approach. A significant gradient between rhombohedral and tetragonal phase has been observed with 100 nm in-depth resolution. The adequate knowledge of phase variation, and its relation to the fabrication technique, is crucial for the enhancement of PZT electro-mechanical properties. Our methodology and findings open up new perspectives in establishing a relevant quantitative feedback to reach ultimate performance in sol-gel PZT thin films.

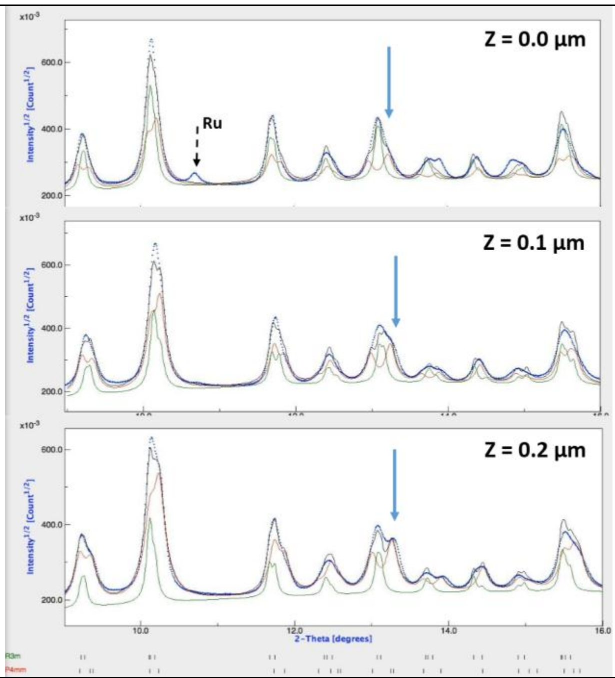

Fig. 2 : Rietveld refinement for Z = 0, 100 and 300 nm (reference is set to the PZT/top electrode interface). Peak splitting due to an increased P4mm ratio is observable in the {103,301 310} peak region (see blue arrows). Inevitable residual Ru peak from top electrode due to beam tail is observed for Z=0.0µm (see dotted arrow).

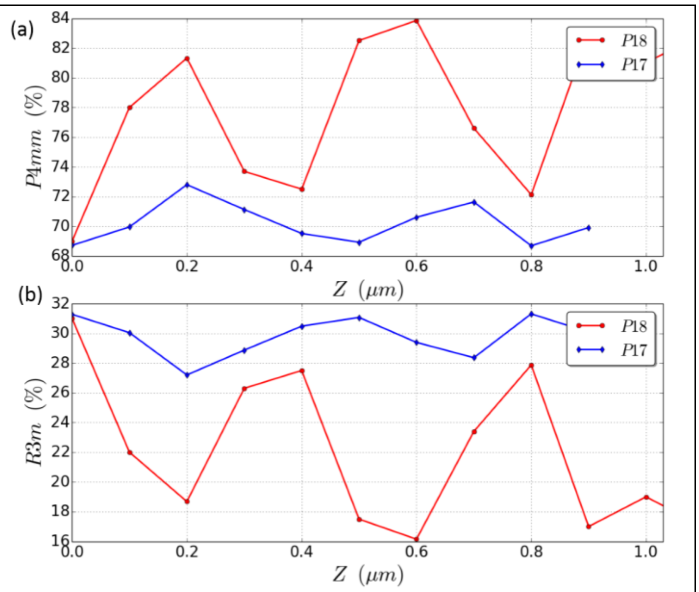

Fig. 3 : Quantitative phase z-profile deduced from Rietveld refinements. P4mm (a) and R3m (b) weight ratio are monitored with a 100 nm in-depth resolution. Optimized sample experiences a 4% residual heterogeneities while the standard one shows up to 12% fluctuations. Periodicity of around 350 nm is clearly observable in both due to sequential aspect of {spin-coated / dry /calcination}{RTA} deposition process.

2. In-situ Results

Thanks to our optimized sample design and efficient instrumentation effort, in-situ loading was very successful. We collect around 500 GB of data . We was able to measure all our samples. Some results are presented below for sample P17. We have similar information for the other samples. We have therefore precious input about physics of our functional film. This will act as an efficient feedback with elaboration process of our devices.

Piezoelectric strain

2D high energy diffraction (transmission geometry) provides numerous information. Averaged piezoelectric tensors is quantified by fitting various peak under different inclination (Fig. 4). We observe typical butterfly loop expected in ferroelectric material.

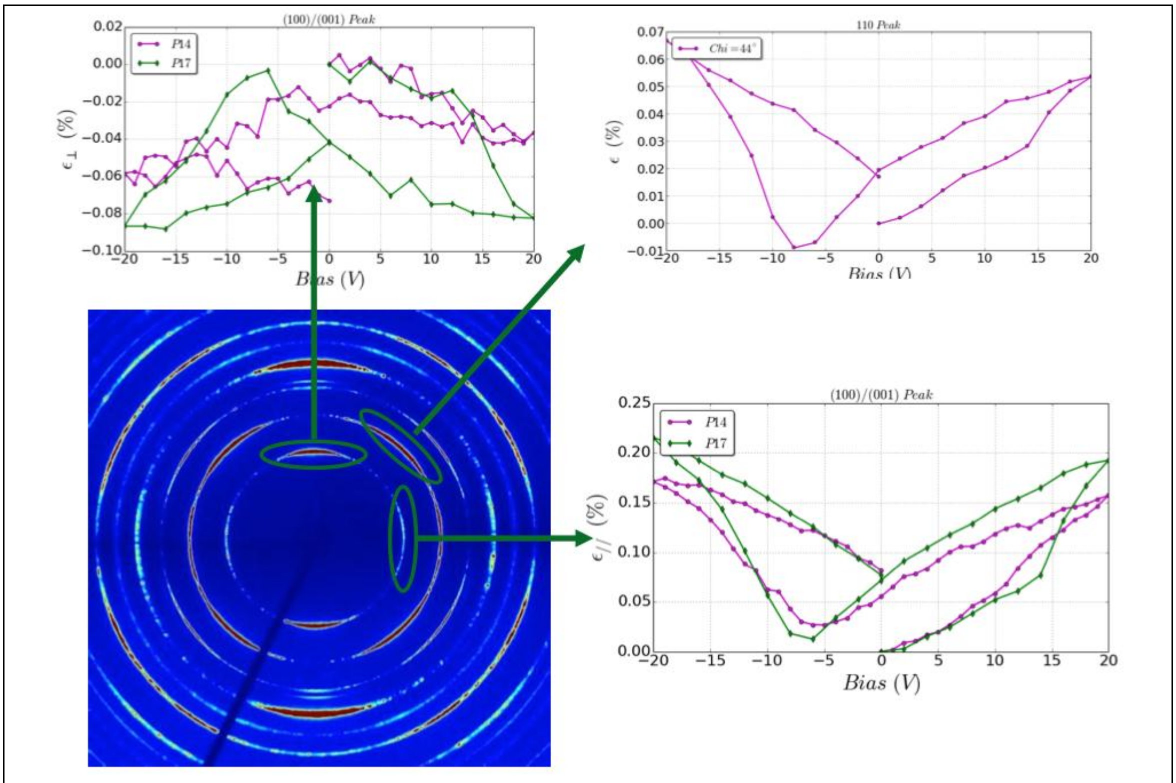

Fig. 4: Piezoelectric strain for different tilts ($\psi = 0°, 45°, 90°$). Butterfly loop heterogeneities are a sign of piezoelectric anaisotropy.

Observation of phase boundary motion

We also observed a significative evolution of R3m phase proportion during the cycles (Fig. 6). This confirms previous observations made on our sample published recently [3].

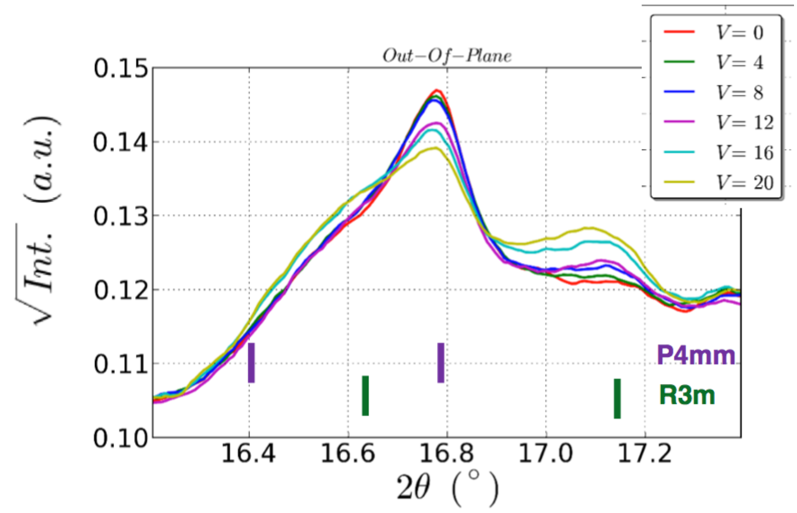

Fig. 5: Detail of (004)/(400) Bragg Peak where an increase of R3m phase proportion is observed during the cycle.

3. Dielectric breakdown

We observed the breakdonw of some of our capacitors during electric loading. We noticed ‘’recovery like’’ behavior in some case or not at all (Fig. 6). Analysis; interpretation, and modeling are under progress.

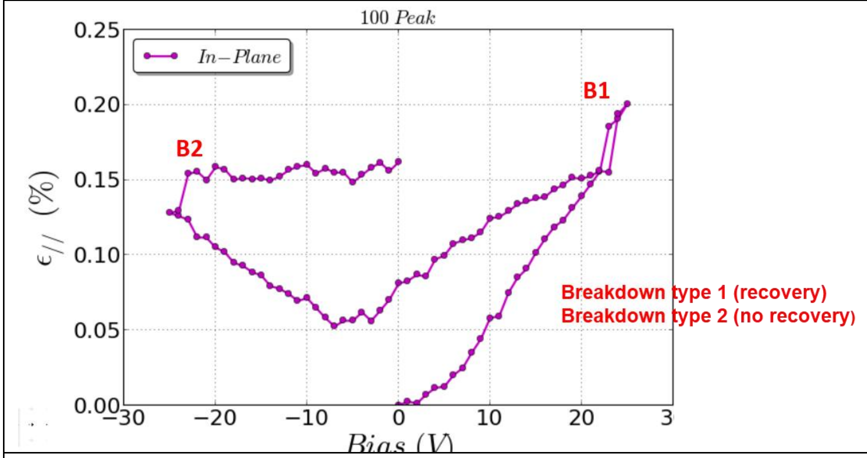

Fig. 6 : Example of electric breakdown observation for sample P18.

Bibliography

[1] N. Vaxelaire *Jour. of Appl. Cryst.* 47, 495–504 (2014).
[2] N. Vaxelaire et al, submitted in *Appl. Phys. Lett.*
[3] V. Kovacova et al, *Phys Rev. B* 90, 140101 (2014)